Ferroelectric properties of (117)- and (001)-oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ polycrystalline thin films

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Highly (117)- and (001)-oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films were fabricated on $Pt/TiO_2/SiO_2/Si(100)$ substrates by chemical solution deposition under the appropriate baking and crystallization conditions. The (117)-oriented BLT films exhibited higher remanent polarization ($2P_r = 24\ \mu C/cm^2$), than did (001)-oriented BLT films, which exhibited only a slight amount of polarization ($2P_r = 6.6\ \mu C/cm^2$). The results of fatigue and retention tests revealed that neither film was fatigued up to 1×10^{10} switching cycles, and the retained charge was unchanged for 1×10^4 s. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1516234]

Ferroelectric thin films have received considerable attention in recent decades for the potential applications in nonvolatile random access memories.[1] Among related materials of interest, lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT) is probably the most extensively studied. PZT films have favorable characteristics, including high polarization, a low processing temperature, and remaining apparently fatigue-free when used conducting oxide electrodes.[2,3] Nevertheless, environmental safety issues concerning the Pb-containing formula may ultimately prevent it from being used in many applications. Layer-structured perovskite like strontium bismuth tantalate ($SrBi_2Ta_2O_9$, SBT) has also been studied.[4] Although SBT is a fatigue-free material, the practical application of SBT is limited, primarily due to its small polarization ($2P_r = 4-16\ \mu C/cm^2$) and high processing temperature (over 750 °C). A recent investigation demonstrated that La-substituted bismuth titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$, BLT) is highly promising for the applications in nonvolatile random access memories.[5] Similar to SBT, BLT films have been reported to be fatigue-free over 3×10^{10} switching cycles, but with much larger polarization ($2P_r = 16-20\ \mu C/cm^2$).[5] Moreover, BLT can be fabricated at temperatures below 650 °C, and is thus compatible with Si-based integrated circuit technology.

BLT is a monoclinic crystal with a lattice constant along the c-axis ($c = 3.289$ nm) that is considerably greater than that along the other axes ($a = 0.542$ nm, $b = 0.541$ nm).[6] The highly asymmetric crystal structure normally promotes the crystallization of BLT films with preferential growth of (001)-oriented grains. Polarization of the resulting (001)-oriented polycrystalline BLT films is likely to be very small because a negligible remanent polarization ($2P_r = 1.1\ \mu C/cm^2$) has been observed from their epitaxial counterparts.[7] Since nucleation with (001) facet is the energy-favorable process, preferential growth of (001)-oriented grains will persist as long as nucleation at the electrode interface is the dominant process. Consequently, methods to change the nucleation pattern must be found to yield non-(001)-oriented BLT films.

Partial pyrolysis may provide a way to change the nucleation pattern of BLT films prepared by chemical solution deposition, including sol-gel and metalorganic decomposition. A significant amount of solvent is known to be left in the film when pyrolysis is incomplete. When the film is subsequently heated to the crystallization temperature, rapid evaporation of solvent may create sites for nucleation in addition to those at the electrode interface. Nucleation at these sites may still yield (001) facet, due to low surface energy, but the resulting nuclei are typically randomly oriented with respect to the film's normal. Hence, non-(001)-oriented films are obtained when the additional nucleation outweighs the nucleation at the electrode interface. In this letter, we report the growth and ferroelectric properties of (117)-oriented, (001)-oriented, and mixed-orientation BLT polycrystalline films prepared by chemical solution deposition under various baking and crystallization conditions.

BLT films were prepared on $Pt/TiO_2/SiO_2/Si(100)$ substrates by chemical solution deposition. The precursor solution for the coating was prepared by dissolving bismuth nitrate, lanthanum nitrate and Ti(diisopropoxide)bis(2,4-pentanedionate) in 2-methoxyethanol at room temperature in the proportion, $Bi_{3.25}La_{0.75}Ti_3O_{12}$, and stabilized with acetylacetone. A 10 mol % excess of bismuth nitrate was added to compensate for possible bismuth loss during the high-temperature process. The precursor solution was spin-coated and baked on the substrate several times to yield the desired thickness of the film (230 nm). For each coating, the films were baked under two different conditions. In the low-temperature baking, films were heated at 175 °C for 5 min. In the high-temperature baking, films were first baked at 175 °C for 5 min, and then baked at 400 °C for another 5 min. All coated BLT films were crystallized at about 700 °C in air for 1 h and were examined using x-ray diffraction (XRD). Electrical characterizations were performed on BLT capacitors of 4×10^{-4} cm^2, as defined by the top Pt electrode. An HP4284 LCR meter determined the dielectric constant and the loss tangent of the films. An RT66A ferroelectric tester took the ferroelectric measurements including those of the hysteresis loop, fatigue, and retention.

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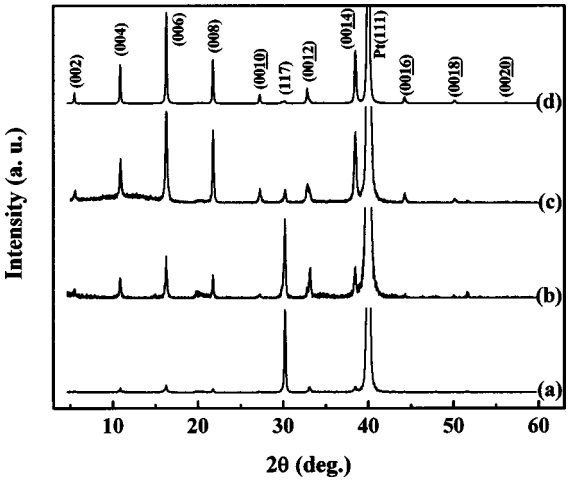

FIG. 1. XRD patterns of BLT films grown on $Pt/TiO_2/SiO_2/Si(100)$ substrates under various conditions; (a) low-temperature baking (175 °C) and 680 °C crystallization, (b) low-temperature baking (175 °C) and 700 °C crystallization, (c) high-temperature baking (400 °C) and 680 °C crystallization, and (d) high-temperature baking (400 °C) and 700 °C crystallization.

The crystallization of coated BLT films was examined using XRD. Although diffraction peaks that corresponded to the perovskite structure were detected at quite a low temperature (~600 °C), they were generally low and broad, indicating poor crystallinity of the films. Above 650 °C, sharp diffraction peaks appeared, and their intensity was found to be sensitive to the baking and crystallization temperatures. Figure 1 shows the XRD results for BLT films prepared under various conditions. In the figure, curves (a) and (b) were obtained from films prepared by low-temperature baking before crystallization, at slightly different temperatures, 680 and 700 °C, respectively. Likewise, curves (c) and (d) were obtained from films prepared by high-temperature baking before crystallization, at 680 and 700 °C, respectively. The XRD results clearly show the trend in the crystallization pattern; that is, a low baking temperature favors the growth of (117)-oriented grains, while a high crystallization temperature favors the growth of (001)-oriented grains. The former can be explained by the extent of pyrolysis induced by the baking. In low-temperature baking, the temperature setting (175 °C) was so low that it mainly served to dry the coating, and most metalorganic compounds may not have decomposed. In contrast, the temperature (400 °C) used in the high-temperature baking was sufficiently high to decompose metalorganic compounds and densify the film, inducing overwhelming nucleation at the electrode interface. The effect of crystallization temperature in this work may have been related to the different growth rates of (117)- and (001)-oriented grains.

Some orientation-sensitive physical properties, such as dielectric constant and ferroelectricity, should vary with the extent of mixing of orientations that is different from one film to the other. To show the effect, the proportion of (117)-oriented grains of each film was roughly estimated with $\alpha = I_{(117)}/(I_{(006)}+I_{(117)})$, where $I_{(117)}$ and $I_{(006)}$ are the peak intensities for (117) and (006) diffractions. For the films considered in Fig. 1, the corresponding α is 0.92, 0.654, 0.126, and 0.024. Figure 2 plots the dielectric constant as a function of frequency for these films. As shown, the dielectric constant is positively correlated with α in the measured frequency range. This observation suggests that polar axis is closer to (117) than (001), which result is consistent with the results observed for epitaxial films. A similar observation has also been reported for bismuth titanate single crystals, for which the dielectric constant measured along the a-axis is approximately double that along the c-axis, and the polar axis for bismuth titanate has been shown to lie at 4.5° from the a-axis.[8,9]

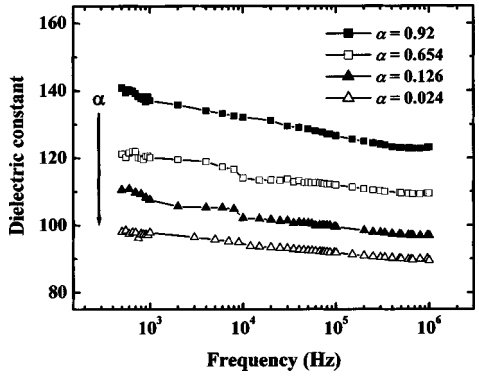

FIG. 2. Frequency dependence of dielectric constant measured from the films used in the previous figure.

A similar correlation between remanent polarization and α has also been observed. Figure 3 shows the $P-E$ hysteresis loops measured from BLT thin films considered above. The measured remanent polarization and coercive field for the (117)-oriented BLT film ($\alpha=0.92$) are 12 $\mu C/cm^2$ and 78 kV/cm, respectively, under a 391 kV/cm maximum applied field. As shown in the figure, both remanent polarization and coercive field decreases as α decreases. For the (001)-oriented film ($\alpha=0.024$), remanent polarization and coercive field is reduced to 3.3 $\mu C/cm^2$ and 55 kV/cm. The higher remanent polarization and coercive field of (117)-oriented films are consistent with that reported for epitaxial BLT films.[7] Nevertheless, the remanent polarization and coercive field for (001)-oriented films exceed those for their epitaxial counterparts ($2P_r=1.1$ $\mu C/cm^2$). A plausible explanation for the difference is that the (001)-oriented film fabricated in this work still contains some (117)-oriented grains, as indicated by the nonzero value of α, which is, however, fairly small (0.024).

The fatigue characteristics of the BLT films at room temperature were also examined. Figure 4 plots the switched

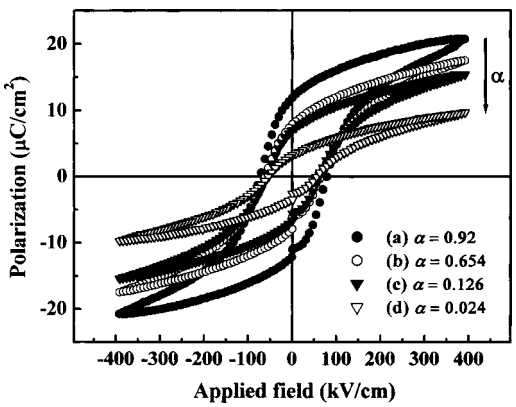

FIG. 3. $P-E$ hysteresis loops of the same BLT films.

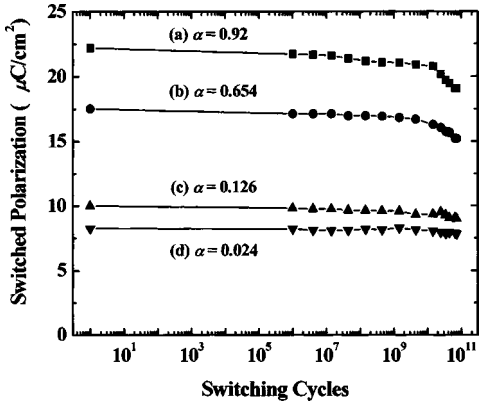

FIG. 4. Fatigue characteristics of BLT films under bipolar pulses of ± 3 V and a measuring voltage of 5 V at 1 MHz.

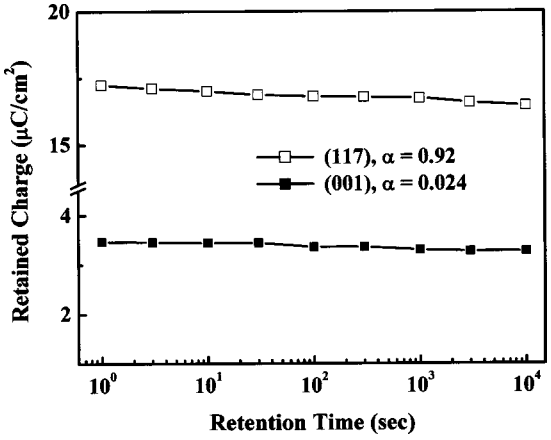

FIG. 5. Retention characteristics of (117)-oriented and (001)-oriented BLT capacitors at room temperature. The retained charge is defined as the average of $(P_{sw}-P_{ns})$ from positive and negative polarity.

polarization as a function of the number of switching cycles, as determined using bipolar pulses of ± 3 V (± 130 kV/cm) and a measuring voltage of 5 V at 1 MHz. In the figure, the switched polarization was calculated from the difference between switching polarization P_{sw} and nonswitching polarization P_{ns}. For all films considered here, the switched polarization maintains without appreciable degradation to 1×10^{10} switching cycles. Nevertheless, under a given switching condition, a greater switched charge seems to correspond to greater degradation. Figure 5 shows the retention characteristics, particularly for the (117)-oriented and (001)-oriented films. As shown, the retained charge, which is the average of $(P_{sw}-P_{ns})$ from the positive and negative polarity, was fairly independent with time, up to 1×10^4 s, for both (117)- and (001)-oriented BLT films. Due to the dielectric relaxation, the retained charge is generally less than the switched charge $2P_r$ measured from the $P-E$ hysteresis, and the difference between them should be as small as possible to maintain enough margin between the digits ''1'' and ''0''. For BLT films fabricated in this work, the ratio of the retained charge to $2P_r$ was close to 90%, significantly higher than for PZT ($\sim$46%).[10]

In summary, polycrystalline $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films were grown on $Pt/TiO_2/SiO_2/Si(100)$ substrates by chemical solution deposition. Depending on the baking and crystallization conditions, (117)-oriented, (001)-oriented, and mixed-orientation BLT films were derived. The dielectric constant and remanent polarization of (117)-oriented considerably exceeded those of (001)-oriented films. All films were shown with favorable fatigue resistance and charge retention.

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